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THERMAL CONDUCTIVITY AND COMPOSITION PROFILE OF A CHEMICALLY REACTING GAS MIXTURE PLACED IN A HOT-WIRE CELL

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ABSTRACT. A simple method is given for obtaining the actual compositions at the hot and the cold surfaces of a hot-wire thermal conductivity cell in which a chemical reaction of intermediate rate is proceeding. These compositions are related to the rates of formation (R_f) and destruction (R_d) of a particular species involved in the chemical reaction. ($R_f - R_d$) is a measure of the departure of the system from the condition of local chemical equilibrium.

INTRODUCTION

The heat flux in a chemically reacting gas mixture placed in a thermal conductivity cell can be divided into two parts, viz., (1) the usual flux in the absence of chemical reactions and (2) the heat flux due to diffusional transport of chemical enthalpies of the reactants and the products. If the reaction rates are so fast that the composition at every point in the conductivity cell is at equilibrium with the local temperature, the thermal conductivity of the reacting gas mixture may be written as (Butler and Brokaw, 1957)

$$\lambda_e = \lambda_f + \lambda_R \qquad \ldots \quad (1)$$

where λ_f is the thermal conductivity of the 'frozen' (absence of chemical reaction) mixture and λ_R, the contribution due to chemical reaction. A generalised expression for λ_R in this case has been obtained by Butler and Brokaw (1957) and further simplified by Brokaw (1960). Again if the reaction is very slow, it has been shown by Secrest and Hirschfelder (1961) that the composition in the cell becomes almost uniform and the contribution of λ_R to the total thermal conductivity is negligible.

It is most difficult to tackle theoretically the problem of heat conduction when the reaction rate is intermediate. In this case, the heat conductivity becomes a function of the reaction rate and the geometry of the apparatus. Consequently for such a system the usual term 'coefficient of thermal conductivity' has no significance. However, we can still talk about an 'effective thermal conductivity' for such a system placed in a thermal conductivity cell. For such a system an elaborate treatment has been given by Brokaw (1961) which permits an evaluation of the 'effective co-efficient of thermal conductivity' of a reacting gas mixture when the temperature difference between the hot and the cold surfaces of the

conductivity cell is not large (e.g. in a hot-wire cell). When there is local chemical equilibrium, the rates R_f, R_d of the formation and the destruction, respectively, of a particular species involved in a chemical reaction, are equal. When the reaction rate is not fast enough to maintain the condition of local chemical equilibrium, $R_f \neq R_d$, and the magnitude of the quantity $(R_f - R_d)$ is a measure of the departure of the system from local chemical equilibrium. $(R_f - R_d)$ can be expressed in terms of the actual compositions in the conductivity cell which are different from the local chemical equilibrium compositions. However, from Brokaw's formulation (1961), it is not possible to find directly the actual compositions and effects of relaxation of chemical energy remain obscure. Secrest and Hirschfelder (1961) have attempted to obtain the composition profile in a conductivity cell. However, their method is suitable in cases where there is a large temperature difference in the cell and it also requires laborious numerical techniques.

In the present paper we have attempted to give a comparatively simple method of obtaining the actual compositions of a reacting gas mixture at the hot and the cold surfaces of a hot-wire cell. Experiments performed on the basis of this method are expected to throw some direct light on the actual physical conditions in the cell in which a reacting gas mixture has been placed.

THEORETICAL CONSIDERATIONS

We shall limit our present considerations to a unimolecular dissociation reaction given by,

$$B \rightleftarrows 2A \qquad \ldots \quad (2)$$

placed in a hot-wire thermal conductivity cell. We shall designate the quantities corresponding to the species B without any suffix and those corresponding to species A by the suffix A. Let G_i denote the molar flux of the species i crossing unit length of a cylinder of radius r. Then, at equilibrium,

$$G_A = -2G \qquad \ldots \quad (3)$$

For the present case, the equations of multi-component diffusion can be written as

$$2\pi r \frac{dx}{dr} = (nD)^{-1}(xG_A - x_A G) \qquad \ldots \quad (4)$$

D is the binary diffusion coefficient between B and A and $n = p/RT$. From Eq. (3) and since $x + x_A = 1$, we get

$$2\pi r \frac{dx}{dr} = -(nD)^{-1}(1+x)G \qquad \ldots \quad (5)$$

and

$$2\pi r \frac{dx_A}{dr} = (nD)^{-1}(1+x)G \qquad \ldots \quad (6)$$

Eqs. (5) and (6) give

$$\frac{dx}{1+x} = -\frac{(nD)^{-1}}{2\pi} G \frac{dr}{r} \qquad \ldots \quad (7)$$

When the reaction is fast enough so that the condition of local chemical equilibrium is valid, the heat flux through unit length of the hot-wire cell is given by

$$q = 2\pi\lambda_e \frac{(T_H - T_C)}{\ln r_C/r_H} \tag{8}$$

where r_C, r_H are the radii of the cell and the hot-wire respectively and T_C and T_H are the temperatures of the walls of the cell. We shall neglect temperature jump at the walls of the cell and surface chemical reactions.

However, if the local chemical equilibrium condition does not hold, the actual heat flux q^* is less than q and we have

$$q^* = 2\pi\lambda^* \frac{(T_H - T_C)}{\ln r_C/r_H} \tag{9}$$

where λ^* is the effective value of the thermal conductivity for the particular cell.

The heat flux q may also be represented as (Secrest and Hirschfelder, 1961),

$$q = -2\pi r\lambda_f \frac{dT}{dr} - GQ \tag{10}$$

where Q is the heat of reaction. By using Eqs (7), (9) and (10) and integrating between the hot and the cold surfaces of the cell, we get

$$\lambda_e(T_H - T_C) = \lambda_f(T_H - T_C) + \frac{Q}{\Delta} \ln\left(\frac{x_{Ce}+1}{x_{He}+1}\right) \tag{11}$$

and

$$\lambda^*(T_H - T_C) = \lambda_f(T_H - T_C) + \frac{Q}{\Delta} \ln\left(\frac{x_C+1}{x_H+1}\right) \tag{12}$$

where $\Delta = (nD)^{-1}$. The subscript e denotes the local chemical equilibrium value. Combining Eqs. (11) and (12) and denoting $\lambda_e - \lambda^* = \Delta\lambda$ we have

$$\Delta\lambda(T_H - T_C) = \frac{Q}{\Delta}\left[\ln\left(\frac{x_{Ce}+1}{x_{He}+1}\right) - \ln\left(\frac{x_C+1}{x_H+1}\right)\right] \tag{13}$$

Eq. (13) expresses the difference between the effective coefficient of thermal conductivity and λ_e in terms of the actual and the local chemical equilibrium compositions at the walls of the cell.

In the reaction

$$B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2A \tag{14}$$

where k_f and k_r are the rate constants we have

$$R_f = k_f x \frac{p}{RT}$$

$$R_d = k_r(1-x)^2 \frac{p^2}{R^2T^2} \tag{15}$$

Therefore, for example, at the hot surface of the cell,

$$(R_f - R_d)T_H - k_r \frac{p}{RT}\left[K_C x_H - \frac{p}{RT}(1-x_H)^2\right] \quad \ldots (16)$$

Thus if we know x_H and T_H the quantity $(R_f - R_d)$ can be directly obtained. As stated earlier, for local chemical equilibrium $R_f = R_d$. Thus the magnitude of $(R_f - R_d)$ will be a measure of the departure of the system from the condition of local chemical equilibrium.

DETERMINATION OF THE ACTUAL COMPOSITIONS AT THE WALLS OF THE THERMAL CONDUCTIVITY CELL

Let the bath temperature T_C be kept constant and the temperature of the hot-wire be varied slightly from $(T_H)_1$ to $(T_H)_2$. Then from Eq. (13)

$$\Delta\lambda_1[(T_H)_1 - T_C] = \frac{Q}{\Delta}\left(ln\,\frac{x_{Ce1}+1}{x_{He1}+1} - ln\,\frac{x_{C1}+1}{x_{H1}+1}\right) \quad \ldots (17)$$

$$\Delta\lambda_2[(T_H)_2 - T_C] = \frac{Q}{\Delta}\left(ln\,\frac{x_{Ce2}+1}{x_{He2}+1} - ln\,\frac{x_{C2}+1}{x_{H2}+1}\right) \quad \ldots (18)$$

the subscripts 1 and 2 correspond to $(T_H)_1$ and $(T_H)_2$ respectively. In a hot-wire cell the difference between T_C and T_H is not large and $(T_H)_1$ and $(T_H)_2$ are also quite close to each other so that it is reasonable to assume that

$$(x_{Ce1} - x_{C1}) = (x_{Ce2} - x_{C2}) \quad \ldots (19)$$

$$(x_{He1} - x_{H1}) = (x_{He2} - x_{H2}) \quad \ldots (20)$$

Since T_C is kept constant, $x_{Ce1} = x_{Ce2}$,

or $$x_{C1} = x_{C2}. \quad \ldots (21)$$

Thus by knowing $\Delta\lambda_1$, $\Delta\lambda_2$, x_{Ce1}, x_{He1}, x_{He2} and using Eqs. (20), (19) and (21) x_C and x_H values can be obtained from Eqs. (17) and (18). The equilibrium compositions can be calculated from the experimentally determined equilibrium constants. The values of $(R_f - R_d)$ can be obtained from Eq. (16).

Experiments on the system $N_2O_4 \rightleftarrows 2NO_2$ by utilising the method described above are in progress.

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